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A Simple Chemical Procedure for Extending the Conductive State of Polypyrrole to More Negative Potentials

by

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**A SIMPLE CHEMICAL PROCEDURE FOR EXTENDING THE CONDUCTIVE STATE
OF POLYPYRROLE TO MORE NEGATIVE POTENTIALS**

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Abstract

The electronically conductive polymer polypyrrole is an electronic conductor at potentials positive of ca. -0.4 V vs. the saturated calomel electrode (SCE) and an electronic insulator at potentials negative of this value. As a result of this potential-dependent conductor/insulator transition, a polypyrrole film can be used as an electrode for redox couples with E° 's positive of ca. -0.4 V vs. SCE but cannot be used as an electrode for couples with E° 's negative of this value. We have discovered a simple chemical procedure that extends the conductive state of polypyrrole to ca. -1.1 V vs. SCE. This procedure entails treating the polypyrrole film with aqueous sodium hydroxide. We demonstrate this extension of the conductive state to more negative potentials in this paper. We also propose, and test, a chemical model that explains the extension of the conductive state.

INTRODUCTION

Electronically conductive polymers can be electrochemically switched between electronically insulating and electronically conductive states [1-5]. This insulator/conductor conversion process is essential to many of the proposed applications of these polymers [5]. However, the conductor-to-insulator transition means that in a certain potential window, these polymers are electronic insulators [1-4]. This is a potential drawback in applications where electronic conductivity is required. As an example, consider the use of a polypyrrole film as an electrode in an electrochemical experiment [4]. Because polypyrrole is an electronic insulator at potentials negative of ca. -0.4 V (vs. the saturated calomel electrode (SCE) in acetonitrile) [1-4], the film could not be used as an electrode for redox couples with E° 's negative of this potential [4].

It would be useful, in such electrochemical applications, if the potential window over which the polymer is conductive could be extended to more negative values. In principle, this could be achieved if the polymer reduction wave could be shifted to more negative potentials. We have recently discovered a simple chemical method that shifts the reduction wave for polypyrrole approximately 0.9 V negative of the value for a conventional polypyrrole film. As a result, the polymer remains in its conductive state to potentials as negative as -1.1 V vs. SCE. This method entails treatment of the polypyrrole film with aqueous NaOH. We demonstrate this extension of the conductive state to more negative potentials in this paper. We also propose, and test, a chemical model that explains the extension of the conductive state.

EXPERIMENTAL

Materials and Equipment. Tetraethylammonium tetrafluoroborate (99% Aldrich) was recrystallized from methanol and dried in vacuo prior to use. 1,2-dihydroxyanthraquinone (Aldrich) was purified by vacuum sublimation. Pyrrole (99%, Aldrich) was distilled under N_2 prior to use. Acetonitrile (UV grade, Burdick and Jackson) and NaOH (Baker) were used without further purification. Gold interdigitated microarray electrodes were obtained from AAI-ABTECH (IME 1550-M, Yardley, PA). SnO_2 -coated glass was donated by Libbey Owen Ford Glass. Platinum disk working electrodes were constructed as described previously [2]. Conventional one compartment electrochemical cells were used; the counter and reference electrodes were a platinum flag and an SCE, respectively. The electrochemical instrumentation has been described previously [2]. The film resistance measurements [2,6] and all other electrochemical experiments were conducted in degassed 0.2 M Et_4NBF_4 in acetonitrile.

Polypyrrole Film Deposition. Polypyrrole films were synthesized electrochemically on Pt disk electrodes [2]. The polymerization solution was 0.5 M in pyrrole and 0.2 M in Et_4NBF_4 ; the solvent was acetonitrile. The polymerization solution was degassed before use by purging with N_2 . A current density of 1 mA cm^{-2} was used during the polymerization. Electrodes of 0.5 cm^2 area were used for most experiments. For electrodes of this area, a total polymerization charge of 28.5 mC was used to synthesize the polypyrrole films. This yields a 0.15 μm -thick film; our methods for determining film thickness are described in [2]. Pt disks of smaller area (0.178 cm^2) were used for some of the studies. The polymerization conditions used for these smaller electrodes were identical to those described above except that the total polymerization charge was 33.8 mC; this resulted in a 0.5 μm -thick film [2].

Finally, large area films were synthesized and sent out for commercial elemental analyses. These films were synthesized on 10 cm² SnO₂-coated glass electrodes. A total polymerization charge of 76.0 C was used; this yields films ca. 20 μm in thickness (2). Two different treatments were employed prior to elemental analysis. One film (the control) was simply rinsed with acetonitrile, dried in vacuo at 100° C for 3 hours, and sent off for elemental analysis. The second film (hydroxide-treated) was treated with hydroxide, in a fashion analogous to that described below; the film was then rinsed with water and acetonitrile, dried and sent out for elemental analysis.

Chemical Treatment for Extension of the Conductive State to More Negative Potentials. The treatment entails immersion of the freshly-synthesized polypyrrole film into degassed 0.2 M NaOH for 10 minutes. Following this treatment, the film was rinsed with water and then with acetonitrile. The resulting "hydroxide-treated" film was then immersed into degassed supporting electrolyte solution for in situ resistance measurements and other electrochemical experiments.

As indicated in the above discussion, two types of polypyrrole films are described in this paper. We will refer to a polypyrrole film that has *not been treated with hydroxide* as a "conventional" film. Films that have received the hydroxide treatment are referred to as "hydroxide-treated" films.

Measurement of Film Resistance. Film resistance was determined using the microelectrode array. This array has 50 pairs of band-shaped electrodes. Each electrode is 15 μm wide by 5 mm long; the separation distance is 15 μm. Polypyrrole was electrochemically polymerized across the surface to interconnect the electrodes. The polypyrrole film was deposited from an

acetonitrile solution containing 0.5 M pyrrole and 0.2 M Et₄NBF₄. The current density was 1 mA cm⁻² of electroactive area (0.075 cm²) and the polymerization charge was 0.285 C.

Film resistance was measured using a previously described method [3,6]. Briefly, the polypyrrole-coated microelectrode array was immersed into 0.2 M Et₄NBF₄ in acetonitrile and the potential was held at the desired value (vs. SCE) using a bipotentiostat. While under this potential control, a small potential (10-100 mV) was applied across the array using the bipotentiostat. The resulting current was measured. The film resistance was then calculated by dividing the applied potential by the resulting current. Film resistances were measured at applied potentials of +0.2 V and -0.8 V where conventional polypyrrole is in its conductive and insulating states, respectively.

RESULTS AND DISCUSSION

The most direct way to show that the conductive state of hydroxide-treated polypyrrole is extended to more negative potentials (relative to conventional polypyrrole) is via measurements of the resistance of the film. We present these data first. We then use cyclic voltammetry to confirm the extended conductive state and to explore the electrochemistry of this phenomenon. Finally, we use these data plus the results of elemental analyses to propose a chemical explanation for the extended conductive state.

Film Resistance. Figure 1 shows a cyclic voltammogram for a conventional polypyrrole film in 0.2 M Et₄NBF₄ in acetonitrile. The redox wave for the polymer is observed at ca. -0.2 V. The oxidized (doped) form of polypyrrole is a good electronic conductor; the reduced (undoped) form is an electronic insulator [1-4]. This change in conductivity is reflected in the in situ resistance data shown in Table I. The conventional polypyrrole film shows low resistance at an

applied potential of 0.2 V (positive of the redox wave) but very high resistance at an applied potential of -0.8 V (negative of the redox wave). The hydroxide-treated film shows an identical low resistance at the positive applied potential (Table I). However, in contrast to the conventional film, *the resistance of the hydroxide-treated film remains low at the negative applied potential of -0.8 V*. These data clearly show that the hydroxide-treated polymer is highly-conductive in this negative potential region where the conventional film is an insulator.

Cyclic Voltammetry. It is well known that anomalously-large capacitive currents are observed in the polypyrrole voltammogram throughout the potential window where the polymer is conductive [1-3,6-9]. These currents can be seen at potentials positive of the polymer redox wave in Figure 1. We have discussed the origins of these large capacitive currents in our previous papers [1,2,8,9]. The appearance of these large capacitive currents can be used as an indicator that the polymer is in its conductive state [1-3,8,9]. If the in situ resistance data presented in Table I are correct, the voltammogram for the hydroxide-treated film should show large capacitive currents at substantially lower (i.e. more negative) potentials than observed for the conventional polypyrrole film.

Figure 2 shows a cyclic voltammogram for a hydroxide-treated polypyrrole film. Note first that the reduction wave for polypyrrole has been shifted to ca. -1.1 V, ca. 0.9 V negative of the position of this wave for conventional polypyrrole (Figure 1). Furthermore, as predicted, the large capacitive currents, characteristic of the conductive state, persist to potentials as negative as -1.1 V. These data add further support to our contention that the conductive state of polypyrrole can be extended via hydroxide treatment. Furthermore, these data quantify the potential window over which the conductive regime extends for the hydroxide-treated polymer.

Figure 3 shows a cyclic voltammogram of a hydroxide-treated polypyrrole film after *eight hours* of continuous voltammetric scanning over the potential region from +0.2 V to -0.8 V (in 0.2 M Et₄NBF₄, acetonitrile). This potential window is just positive of the reduction wave for the hydroxide-treated film (Figure 2). Note that the large capacitive currents, characteristic of the conductive state, are still observed after this extensive period of electrochemical cycling. We have found that, provided the film is not cycled through the reduction wave (-1.1 V, Figure 2), the film remains in the conductive state. However, if the polymer is repeatedly scanned through the reduction wave at -1.1 V, this reduction wave slowly disappears and the conventional reduction wave at ca. -0.2 V, grows in (see Figure 4).

These studies illustrate the following two important points: 1) The extended conductive state of the hydroxide-treated film can be maintained, for very long times, provided the potential is not scanned through the reduction wave (Figure 3). 2) If the potential is scanned through the reduction wave, the film converts back to a conventional film with conventional conductive state and electrochemistry (Figure 4).

Electrochemistry of 1,2-Dihydroxyanthraquinone (DHA) at Conventional and Hydroxide-Treated Polypyrrole. The voltammetry of DHA can be used to obtain further proof that the conductive state is extended in the hydroxide-treated polymer. Figure 5A shows a cyclic voltammogram of DHA at a bare (uncoated) platinum electrode. Figure 5B shows a voltammogram for the same DHA solution at a Pt electrode coated with a conventional polypyrrole film. Because the reduction wave of polypyrrole is positive of the reduction wave of DHA, the DHA electrochemistry is almost totally blocked by the reduced, insulating polypyrrole film (Figure 5B). (The residual current observed at ca. -0.6 V results from the slow diffusion of DHA

through the polypyrrole film to the substrate Pt electrode [4].) These data clearly illustrate the point made in the introduction - conventional polypyrrole films cannot be used as electrodes for redox couples with E° 's negative of the polymer redox wave [4].

If the hydroxide-treated polymer is, indeed, conductive in the potential window where DHA is reduced (-0.7 V, Figure 5A), the DHA voltammogram should be observable at an electrode coated with the hydroxide-treated film. Figure 6 shows that this is, indeed, the case. The inset in Figure 6 shows a plot of i_{peak} vs. square root of scan rate for the reduction of DHA at the hydroxide-treated polypyrrole film. This plot is linear over the scan rate region employed (10 to 100 mV s^{-1}). This shows that the reduction of DHA is diffusion controlled and is not influenced by adsorption at, or absorption into, the polypyrrole film [10]. Analogous results, for redox molecules with positive E° 's, have been observed at electrodes coated with conventional polypyrrole films [7,10,11]. This is, however, the first time that electrochemistry for a molecule with an E° negative of the polypyrrole redox wave has been observed at a polypyrrole-coated electrode.

Finally, Figure 6 shows that there is a reduction in capacitive current for the hydroxide-treated polypyrrole film when the electrochemistry of DHA is being driven at the surface of this film. An analogous effect was observed by Diaz et al., for redox molecules with positive E° 's, at an electrode coated with a conventional polypyrrole film [10]. They suggest that the redox species acts as a charge-transport agent and dissipates charge in the polypyrrole film [10].

Elemental Analysis Data. Elemental analysis data for both conventional and hydroxide-treated polypyrrole films are shown in Table II. The results obtained are in general agreement with previous analyses of this type on such films [12-15]. Note first that the dopant anion for the

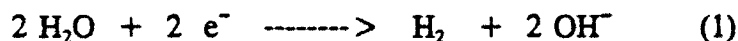
conventional polymer (BF_4^-) is completely removed from the film during hydroxide treatment [12-14]. In addition, the oxygen content of the hydroxide-treated film is higher than for the conventional film [14,15]. These data suggest that exposure of polypyrrole film to aqueous base causes ion exchange of the BF_4^- , initially present in the film, with OH^- from the contacting solution phase [16]. This is supported by the fact that the quantity of BF_4^- lost from the film (0.19 moles per pyrrole ring, as determined from the F element ratio) is identical to the amount of oxygen gained (0.19 moles per pyrrole ring). Finally, it has been demonstrated that such ion exchange processes do occur when polypyrrole films are immersed into solutions containing alternative counterions [17].

This proposed ion exchange process accounts for both the loss of BF_4^- from the film and the increase in film oxygen content (Table II). The alternative explanation for the increase in oxygen content in the hydroxide-treated film is that OH^- hydroxylates the polymer [18]. This would not, however, explain the concomitant loss of BF_4^- . Furthermore, if the hydroxide is covalently-attached, it could not simultaneously act as the dopant anion and there clearly must be a dopant anion or else the film would not be highly conductive (Table I). Finally, we have recently used an in situ infrared method to show that the high oxygen contents observed in *conventional polypyrrole films* (see Table II) are due to covalently-bound hydroxide [19]. This covalently-bound hydroxide results from nucleophilic attack by trace water during polymer synthesis [19]. This explains the high oxygen contents of the conventional films investigated here (Table II).

Finally, as has been observed previously [14], the hydrogen content of the film decreases slightly upon exposure to aqueous base (Table II). This suggests that some deprotonation of the polymer has occurred [12,14,20]. However, even after hydroxide treatment, the H/C ratio is still higher than the theoretical ratio of 0.75. Polypyrrole often contains excess H [14,21]. This excess H results from sp^3 defects in the polymer chain and at the chain ends [14,21].

These data suggest that the primary effect of exposure to aqueous hydroxide *at the concentration level and exposure times used here* is ion exchange of BF_4^- with OH^- from the contacting solution phase. It is important to point out, however, that exposure to higher concentrations of base for longer durations has been shown to dramatically decrease the conductivity of polypyrrole [12-14]. Hence, whether exposure to base causes simple ion exchange or other (more deleterious) chemistries [12-14] clearly depends on the experimental conditions employed.

An Electrochemical Method for Converting Conventional Polypyrrole into Hydroxide-Form Polypyrrole. Consider a polypyrrole film-coated electrode that is immersed in an acetonitrile solution that *contains a low concentration of intentionally-added water*. If the potential of this electrode is scanned to very negative values (e.g. -1.6 V), the water present in the acetonitrile solution will be reduced via



If the ion exchange selectivity for polypyrrole in this solvent is such that OH^- is favored over BF_4^- (see below), the electrochemically-generated OH^- could displace the BF_4^- counterion from

the film and the net result would be a film containing OH^- as the counterion. Hence, this electrochemical procedure should have the same effect on polypyrrole as exposure of the film to aqueous hydroxide solution.

Figure 7 shows that this is, indeed, the case. An electrode coated with a $0.15\text{ }\mu\text{m}$ -thick polypyrrole film was immersed into $0.2\text{ N Et}_4\text{NBF}_4$ in acetonitrile that was also $1\text{ }\%$ (v/v) in water. The potential of the electrode was then repeatedly scanned from 0.2 V to -1.6 V . As shown in Figure 7 a conventional polypyrrole voltammogram is initially obtained; i.e. redox wave at ca. -0.2 V , high capacitive currents positive of this wave and low capacitive currents negative of this wave. However, with repeated scanning, the conventional redox wave at -0.2 V is lost and a new wave at -1.1 V (characteristic of hydroxide-treated polypyrrole, Figure 2) appears. Furthermore, the high capacitive currents characteristic of the conductive state persist at potentials positive of this new redox wave. Ultimately, a voltammogram indistinguishable from the voltammogram for the hydroxide-treated film is obtained.

The voltammograms shown in Figure 7 make two important points. First, they show that the conductive state of polypyrrole can be extended by a simple electrochemical procedure. Second, they add further support for our contention that the extension of the conductive state results from replacement, via ion exchange, of BF_4^- with OH^- . In this case, the OH^- is generated electrochemically (Equation 1).

Chemical Rationale for the Extension of the Conductive State in Hydroxide-Form Polypyrrole.

One final question remains to be answered - why would the electrochemical and electronic properties of the polymer be so different when OH^- is the counterion? The answer to this question lies in the thermodynamics of the anion exchange reactions for the oxidized

(polycationic) form of polypyrrole. Consider the following anion exchange reaction at a polypyrrole film



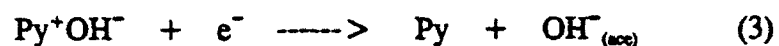
where Py^+ represents a cationic site along the polymer chain and the subscript "acc" denotes an anion in the contacting acetonitrile phase. This reaction describes the exchange of OH^- in the polymer phase with BF_4^- from the contacting solution phase; i.e. the reverse of the reaction of interest to these investigations.

We begin by considering what the data in Figure 3 say about the position of equilibrium for this reaction. Figure 3 shows that polypyrrole that contains OH^- as the counterion (i.e. Py^+OH^-) can be placed into an electrolyte solution that is 0.2 M in BF_4^- and *contains no intentionally-added OH^-* yet the OH^- is not displaced from the film. We know this is true because, if the OH^- were displaced, the film would convert back to a conventional film with conventional redox chemistry. This does not happen unless the OH^- -containing film is reduced (at ca. -1.2 V, Figure 4), thereby driving the OH^- from the film.

These data clearly show that the position of equilibrium for the reaction shown in Equation 2 lies very far to the left or that the standard free energy change for this reaction ($\Delta G^\circ_{\text{rxn2}}$) is a large positive number. This situation is completely analogous to ion exchange reactions involving the displacement of hydrophobic cations from the sulfonated cation exchange polymer Nafion [22]. In analogy to the data in Figure 3, Nafion films containing hydrophobic cations can be placed into (aqueous) solutions containing huge excesses of inorganic cations without displacement of the hydrophobic cation from the film [22]. We have discussed the

chemical basis for Nafion's unusual ion exchange selectivity in some detail [22]. We will discuss the chemical basis for polypyrrole's unusual ion exchange selectivity later. We first show, however, that this unusual ion exchange selectivity is, in fact, responsible for the extension of the conductive state to more negative potentials.

The electrochemistry of the extended conductive state can be described by the following two redox reactions



where Py is the neutralized form of the formerly positively-charged site along the polymer chain. These reactions can be described thermodynamically by the two standard reduction potentials E°_{OH} (Reaction 3) and $E^\circ_{\text{BF}_4}$ (Reaction 4). The experimental data in Figures 1 and 2 clearly show that E°_{OH} lies very negative of $E^\circ_{\text{BF}_4}$. This, on an empirical level, accounts for the extension of the conductive state in the OH^- -form of the polymer.

In fact, the chemistry described by Reactions 3 and 4 and the chemistry described by Reaction 2 are identical. This can be proven by subtracting Reaction 3 from Reaction 4 and rearranging. Reaction 2 is obtained. Thus, the standard free energy change for Reaction 2 ($\Delta G^\circ_{\text{Rx2}}$) is related to the difference in E° 's for Reactions 3 and 4, ΔE° , via

$$\Delta E^\circ = E^\circ_{\text{OH}} - E^\circ_{\text{BF}_4} = -\Delta G^\circ_{\text{Rx2}}/nF \quad (5)$$

The bottom line is that the conductive state in the hydroxide-form polymer is extended to more negative potentials (large negative ΔE° , Equation 5) because the polymer shows tremendous thermodynamic preference for OH^- relative to BF_4^- (large positive $\Delta G^\circ_{\text{Rx2}}$, Equation 5).

Why does oxidized polypyrrole show such tremendous ion exchange selectivity for OH^- relative to BF_4^- ? The driving force for any ion exchange reaction can be divided into two components - the affinity that the ion has for the polymer and the affinity that the ion has for the contacting solution phase (Equation 2). In conventional ion exchange polymers, the (electrostatic) affinity that the ion has for the polymeric phase dominates ion exchange selectivity and highly-charged (hydrophilic) ions are preferred [23]. In contrast, in Nafion, hydrophobic ions are preferred because water can lower its free energy by expelling such ions and because Nafion offers hydrophobic sites to accommodate such ions [22]. Hence, water pushes hydrophobic ions into the Nafion phase and gladly accepts (solvates) the hydrophilic ions that come out [22].

We believe that solvation in the solution phase also dominates selectivity in the ion exchange process shown in Equation 2. As discussed by Sawyer and Roberts, anions are poorly solvated by aprotic, dipolar solvents because of the absence of hydrogen bonding [24]. As a result, large, polarizable "soft" anions (e.g. BF_4^-) are more strongly solvated than small, electronegative "hard" anions (e.g. OH^-) in such solvents [24,25]. The chemistry of this reversal (relative to water) in the solvation energy order has been discussed in detail by Miller and Parker [25]. This analysis suggests that polypyrrole prefers OH^- over BF_4^- *when acetonitrile is the contacting solution phase* because acetonitrile solvates BF_4^- much more strongly than it solvates OH^- .

This model can be tested experimentally by exchanging an alternative "hard" anion into polypyrrole and investigating the electrochemistry of the resulting film. If our model is correct,

a new redox wave will be observed at potentials negative of the conventional wave. F^- is the obvious choice to use for this test. F^- was exchanged into a conventional (i.e. BF_4^- -containing) polypyrrole film by immersing the film into an aqueous solution of 1.0 M NaF and scanning the potential of the substrate electrode repeatedly through the polymer redox wave (-0.9 V to +0.1 V, 20 mV s⁻¹). After one hour of continuous scanning, the film was rinsed with acetonitrile and returned to a solution of 0.2 M Et₄NBF₄ in acetonitrile.

Figure 8 shows a cyclic voltammogram of the F^- -treated film. In agreement with our prediction, a new, more negative redox wave is, indeed, observed. Hence, these data support our contention that it is the lack of solvation of hard anions that dominates ion exchange selectivity when polypyrrole is immersed into acetonitrile. It is worth noting, however, that the conventional polymer redox wave (ca. -0.2 V) is also observed in the F^- -treated film (Figure 7). This wave also appears because some of the F^- anions are exchanged with BF_4^- when the film is returned to the 0.2 M Et₄NBF₄ solution. This is not surprising since the solution contains a huge concentration of BF_4^- and no F^- . Indeed, that the film retains F^- under these conditions clearly shows that the polymer greatly prefers this anion relative to BF_4^- . Again, this is in complete agreement with our proposed model.

It is worth noting that such large shifts in the redox potential of polypyrrole have not been observed previously because the usual anions employed in polypyrrole electrochemistry (e.g. BF_4^- , ClO_4^- , and PF_6^-) are relatively close in size (0.284, 0.290, and 0.301 nm, respectively) [26] and polarizability and, therefore, have similar (high [25]) solvation energies

in acetonitrile. Finally, the model proposed here also allows for an interpretation of the data shown in Figure 4. Recall that the voltammogram in Figure 4 resulted after a hydroxide-treated film was scanned repeatedly through the new reduction wave at ca. -1.1 V. It was noted that this voltammogram suggests that the hydroxide-treated film had converted back into a conventional film. While OH^- is difficult to remove from the film, once the thermodynamic penalty is paid (i.e. the polymer is reduced at -1.1 V) it does, indeed, come out. Upon voltammetric re-oxidation of the film, charge neutrality can be maintained by either incorporating BF_4^- from the electrolyte or reincorporating the expelled OH^- . Because there is a enormous excess of BF_4^- in solution, repeated scanning through the redox wave ultimately causes BF_4^- to be incorporated and the film becomes (chemically and electrochemically) a conventional film again.

CONCLUSIONS

We have shown that the conductive state of polypyrrole can be extended to very negative potentials via a simple chemical treatment in aqueous NaOH . We have proposed a simple chemical model that explains this extension of the conductive state. From an electrochemical point of view, extension of the conductive state means that a polypyrrole film can be used as an electrode for redox couples with highly-negative E° values (e.g. Figure 6). This could have potentially important implications for applications of this polymer to electrochemical sensors. We are currently exploring this idea.

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Table I. In Situ Polypyrrole Film Resistances

Type of Film	Film Resistance (Ω) At Indicated Potential (V vs. SCE)	
	+0.2 V	-0.8 V
Conventional	18.5	$> 1 \times 10^7$
Hydroxide-Treated	19.0	19.0

Table II. Elemental Ratios From Elemental Analysis^a

Element	Conventional Film	Hydroxide-Treated Film
N	1.00	1.00
C	3.98	4.04
H	3.39	3.25
O ^b	0.65	0.84
F	0.78	<0.01

^a Calculated assuming a ratio of unity for nitrogen

^b Oxygen calculated by difference.

Figure Captions

Figure 1. Cyclic voltammogram for a 0.15 μm -thick "conventional" (see text) polypyrrole film in 0.2 M Et_4NBF_4 in acetonitrile. Scan rate 20 mV/s.

Figure 2. Cyclic voltammogram for a 0.15 μm -thick "hydroxide-treated" (see text) polypyrrole film in 0.2 M Et_4NBF_4 in acetonitrile. Scan rate 20 mV/s.

Figure 3. Cyclic voltammogram of a 0.15 μm -thick hydroxide-treated polypyrrole film after 8 hours of continuous cycling between -0.8 V and + 0.2 V (vs SCE) in 0.2 M Et_4NBF_4 in acetonitrile. Scan rate 20 mV/s.

Figure 4. Cyclic voltammograms for a 0.15 μm -thick hydroxide-treated polypyrrole film after repeatedly scanning between -1.4 V and +0.2 V.

Figure 5A. Cyclic voltammogram of 4.0 mM 1,2-dihydroxyanthraquinone at a bare Pt disk electrode in 0.2 M Et_4NBF_4 in acetonitrile. Scan rate 20 mV/s.

B. Voltammogram analogous to A but at a Pt electrode coated with a 0.15 μm -thick conventional polypyrrole film.

Figure 6. Cyclic voltammogram for 1,2-dihydroxyanthraquinone at a 0.15 μm thick hydroxide-treated polypyrrole film. Scan rate and solution as per Figure 5. Inset - peak

current vs. square root of scan rate for 1,2-dihydroxyanthraquinone at the hydroxide-treated film.

Figure 7. Consecutive cyclic voltammograms for a conventional polypyrrole film ($0.15\ \mu\text{m}$ thick) in $0.2\ \text{M Et}_4\text{NBF}_4$ in acetonitrile that is also 1 (v/v) % in water. Scan rate $20\ \text{mV/s}$. As indicated by arrows, wave at ca. $-0.2\ \text{V}$ is decreasing and wave at ca. $-1.1\ \text{V}$ is increasing. Scan number is indicated for each wave.

Figure 8. Cyclic voltammogram of a $0.5\ \mu\text{m}$ thick-polypyrrole film in $0.2\ \text{M Et}_4\text{NBF}_4$ in acetonitrile. Scan rate $20\ \text{mV/s}$. Film had previously been cycled from $-0.9\ \text{V}$ to $+0.1\ \text{V}$ at $20\ \text{mV/s}$ in $1\ \text{M}$ aqueous NaF for 1 hour.

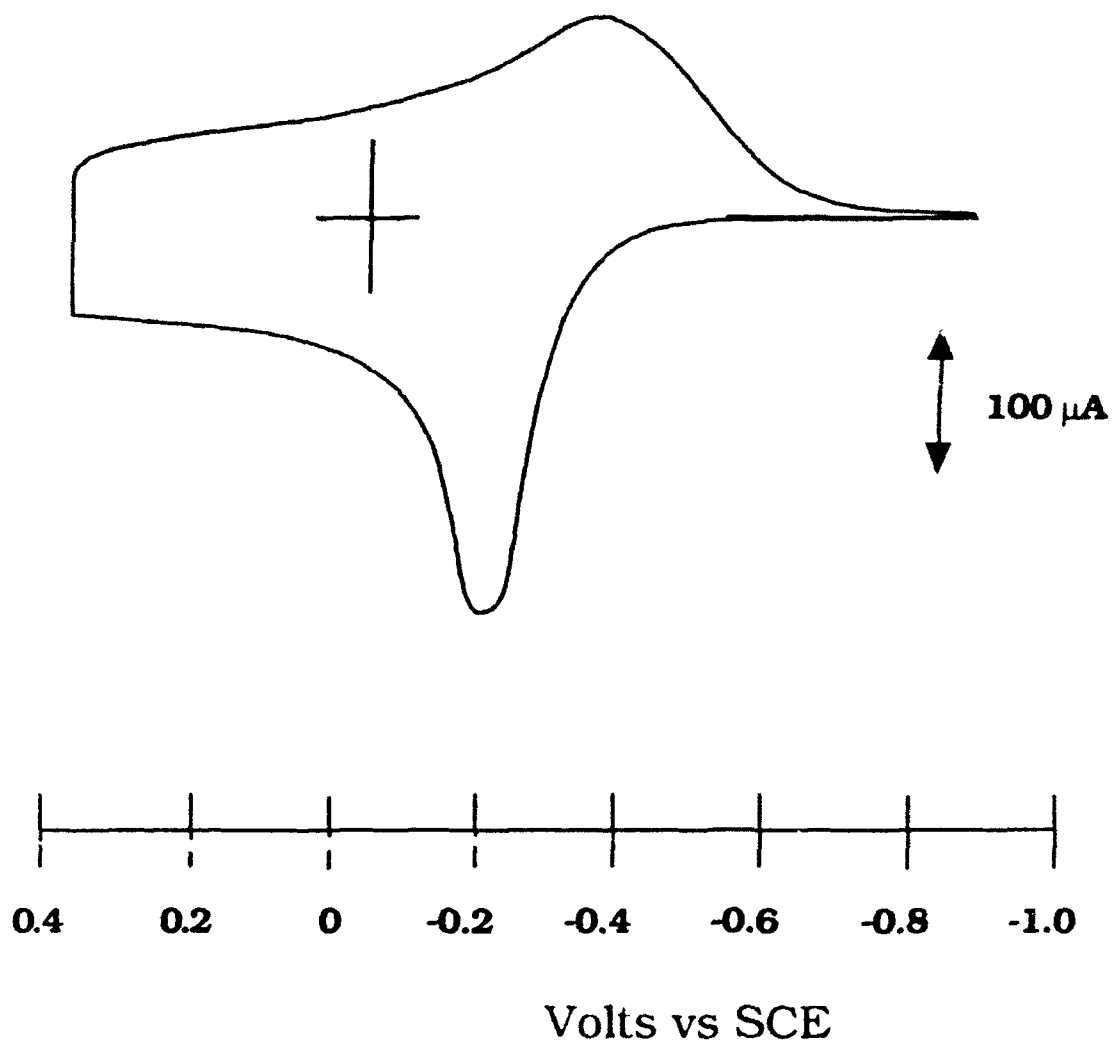


Fig. 1

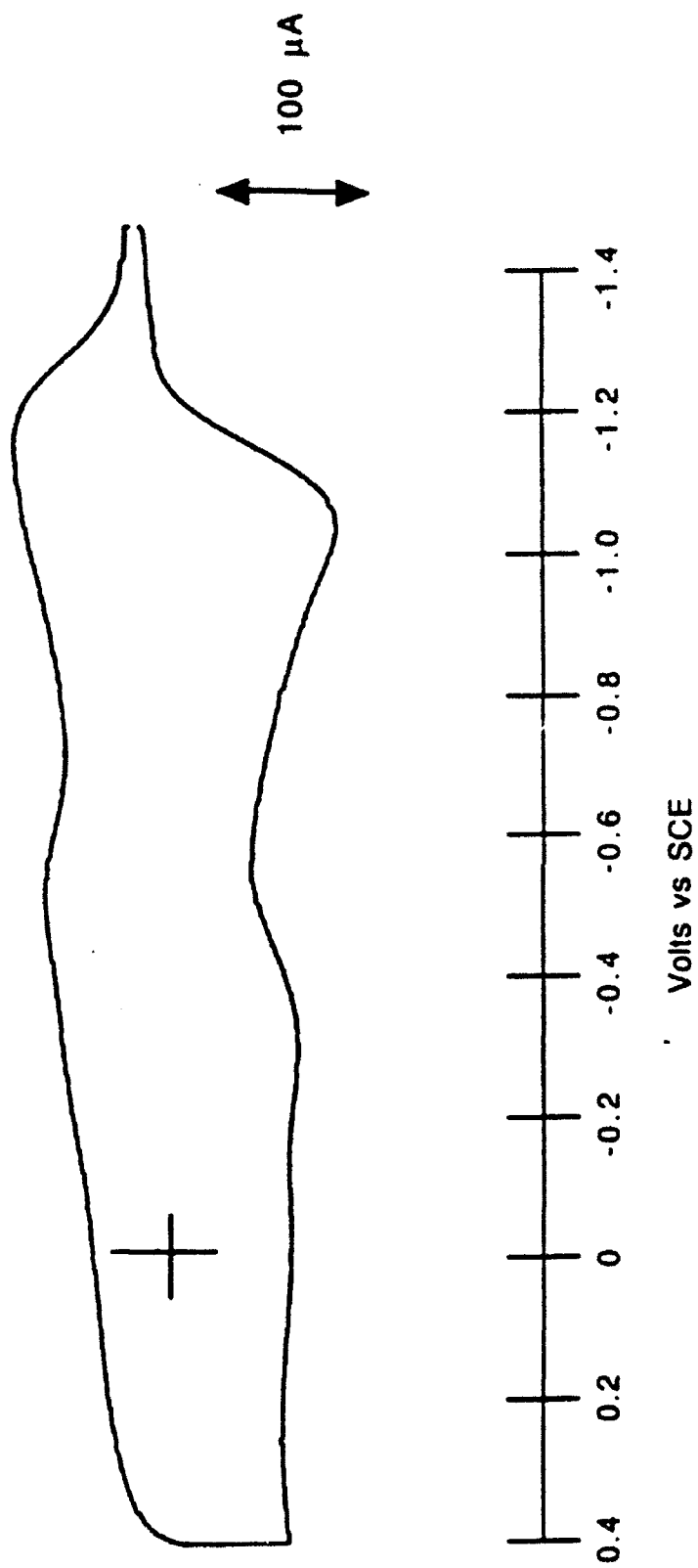


Fig. 2

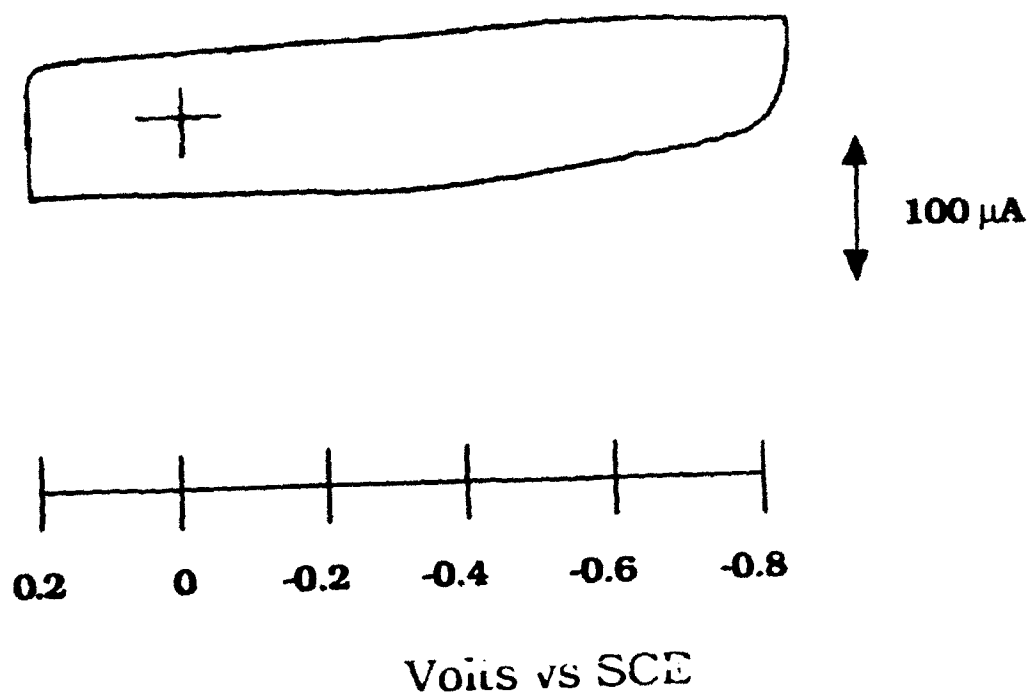


Fig.3

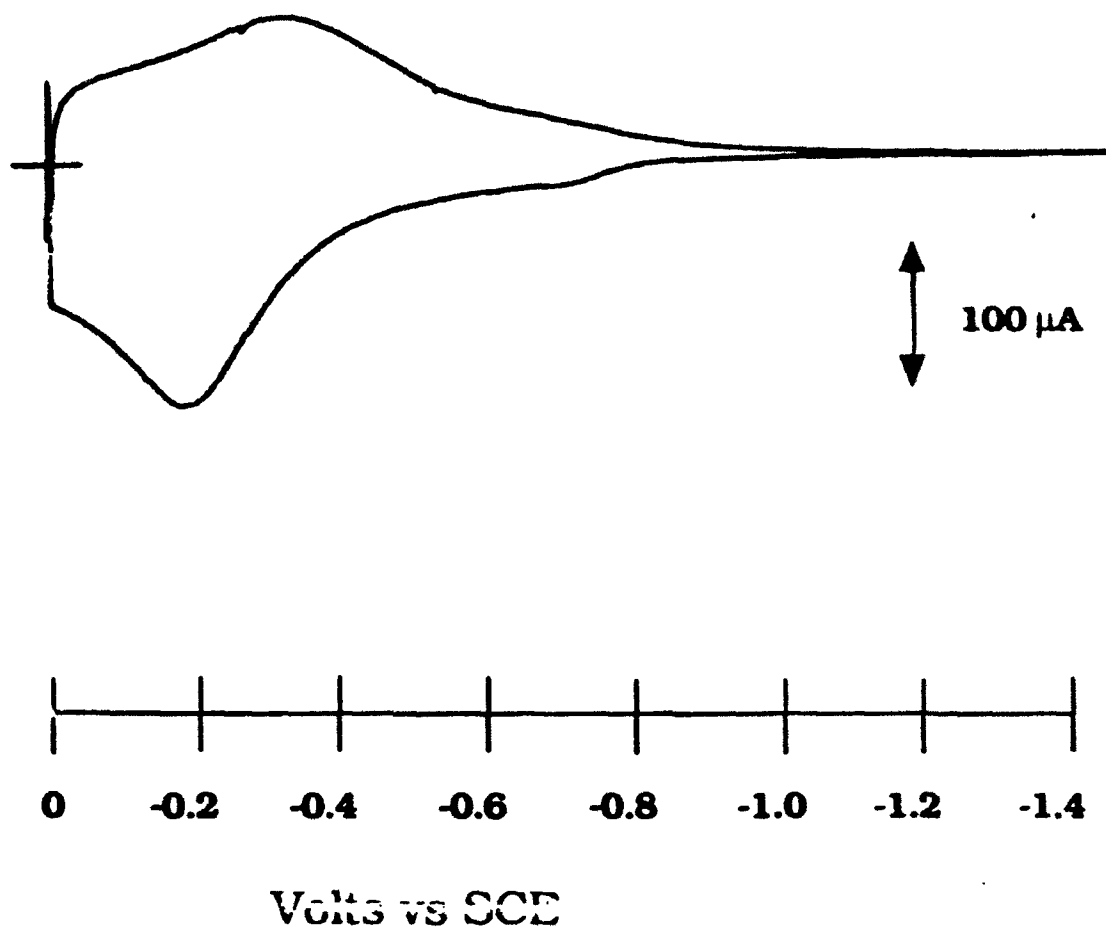
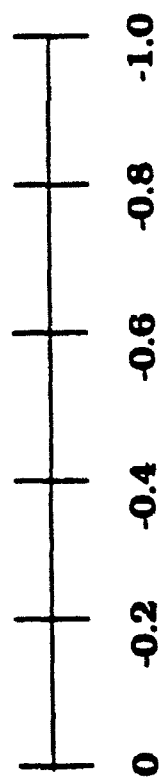
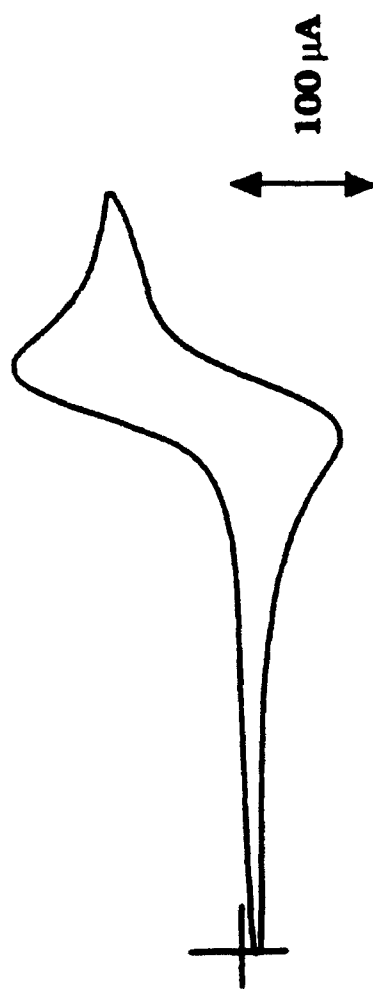


Fig. 4



Volts vs SCE

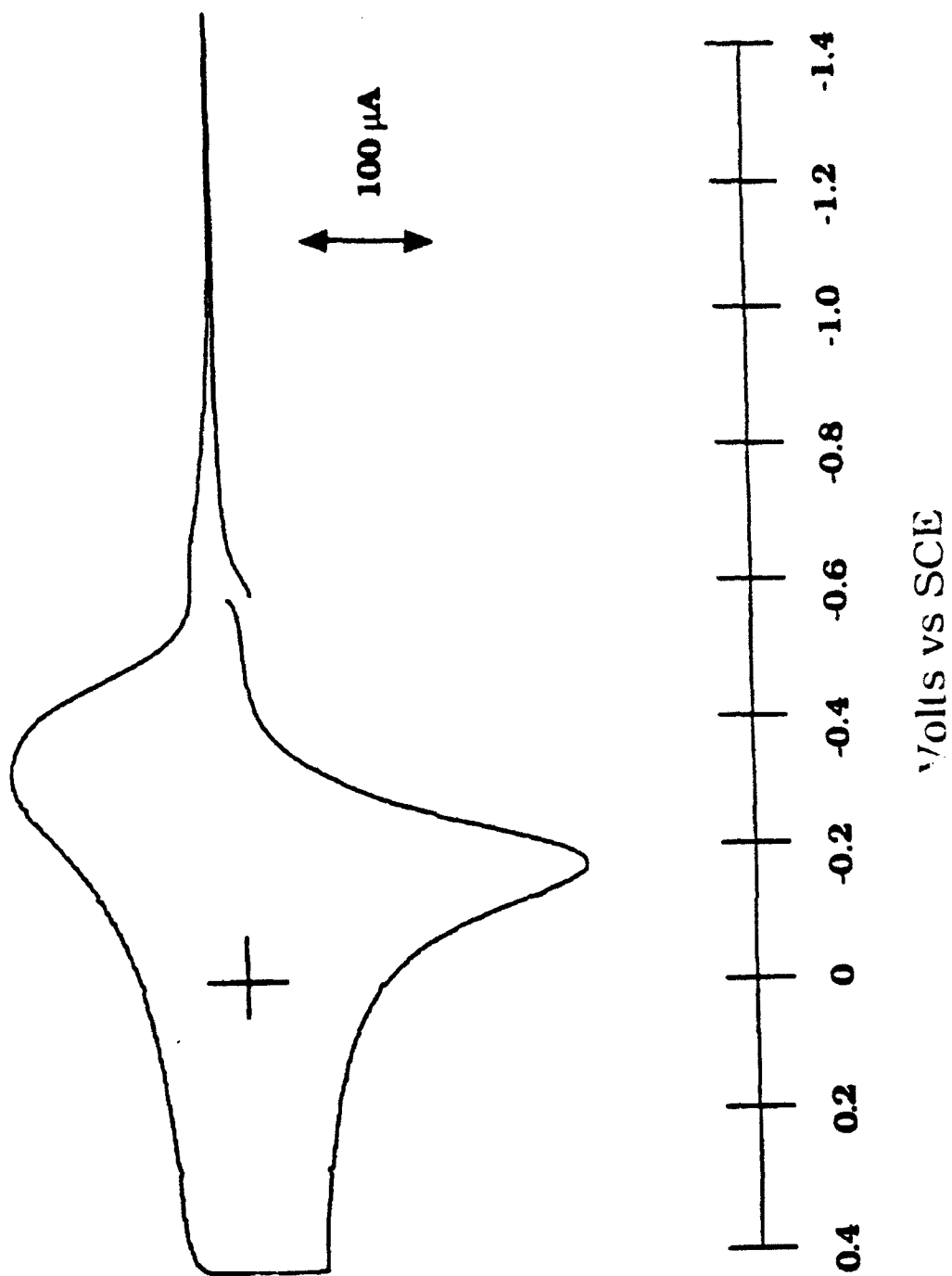


Fig. 5B

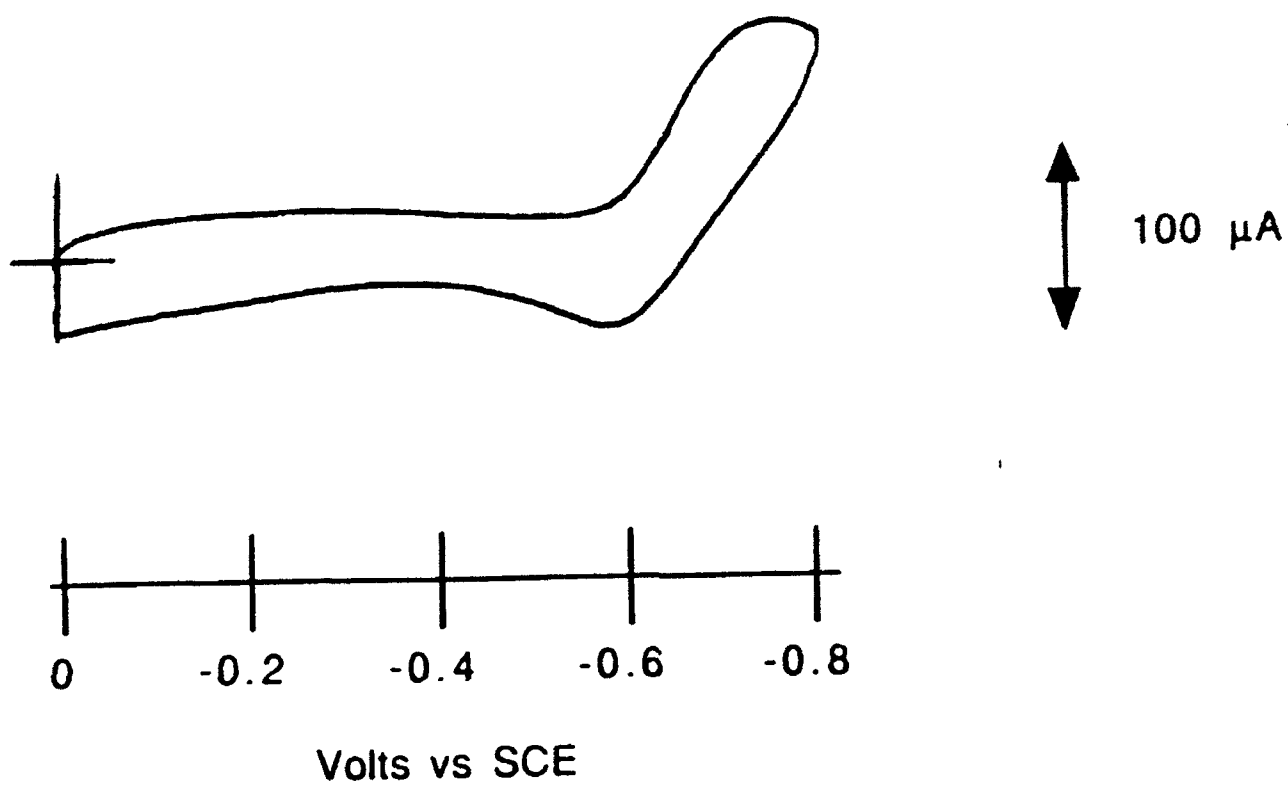


Fig. 6



Fig. 6

INSET

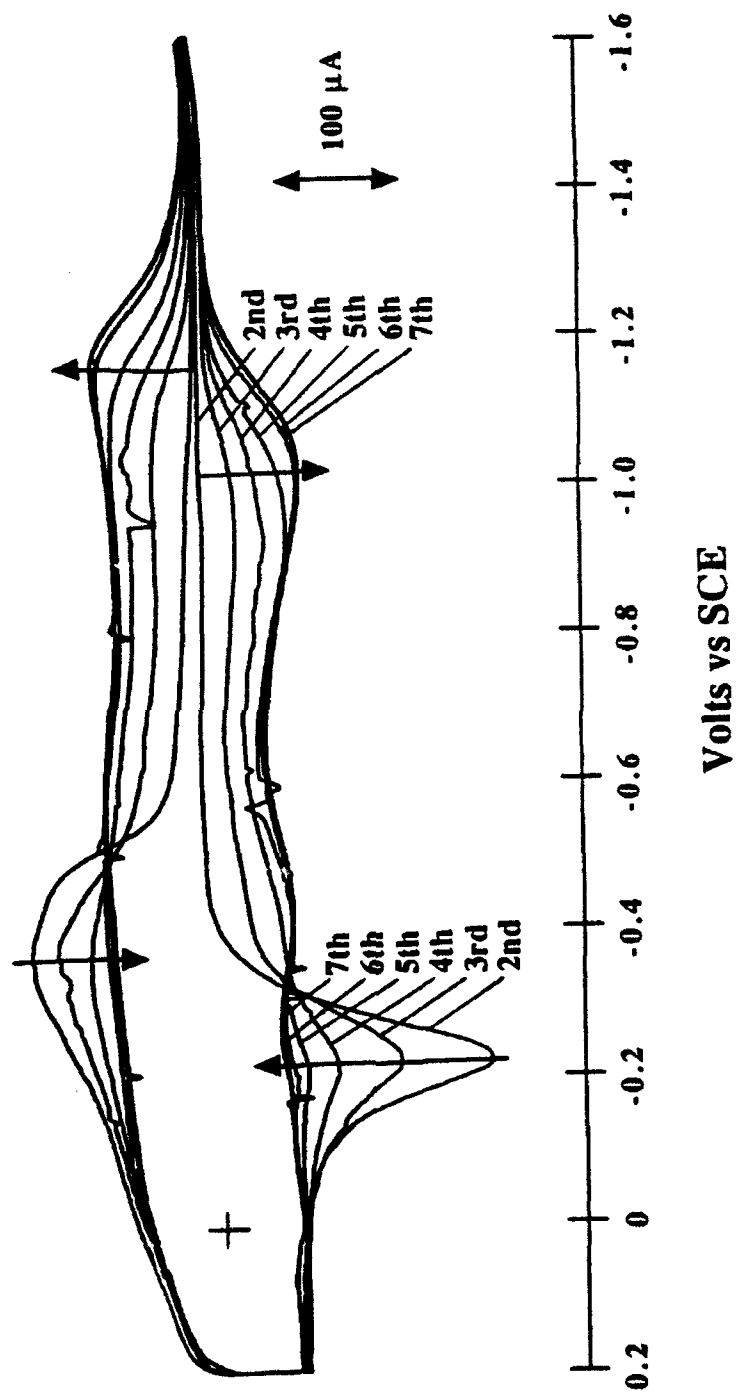


Fig. 7

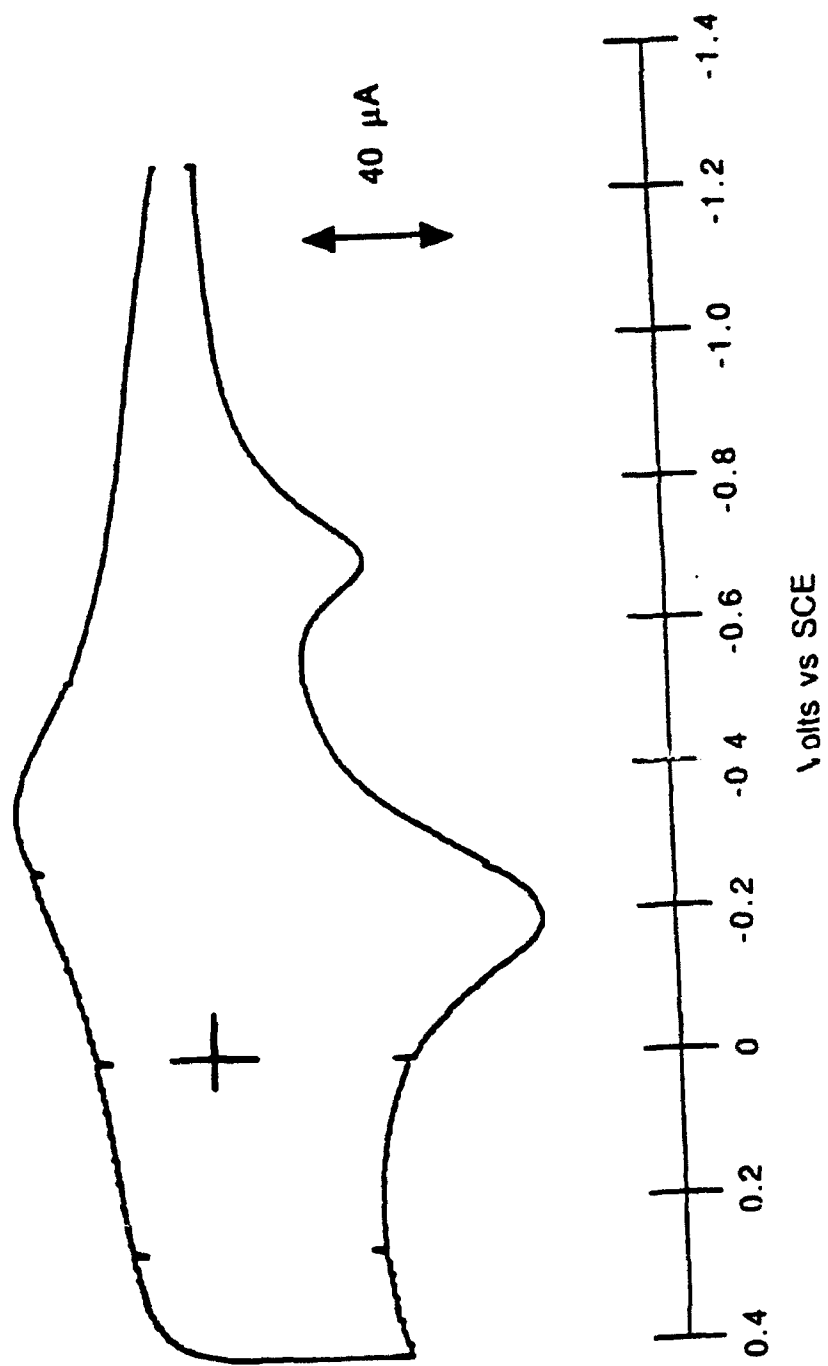


Fig 8